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Ab Initio Study of Si Doped Carbon Nanotubes: Electronic and Structural Properties

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ABSTRACT

We report the electronic and structural properties of silicon doped carbon nanotubes using first principles calculations based on the density-functional theory. In the doped metallic nanotube a resonant state appears about 0.7 eV above the Fermi level and for the semiconductor tube the Si introduces an empty level at approximately 0.6 eV above the top of the valence band.

INTRODUCTION

The new structural form of carbon discovered by Iijima in the early 1990 [1] has attracted the attention of several research groups due to their interesting properties from both a fundamental physics as well as the possible application viewpoint. Single-walled nanotubes, depending on their chirality and diameter, are either a one-dimensional metal or semiconductor [2]. The presence of semiconductor and metallic one-dimensional structures in the same family of materials opens up exciting possibilities of new phenomena and novel device structures. In the recent literature there are reports of several groups that have succeeded in synthesizing doped carbon tubes, using different techniques as arc discharge [3] and gas-phase pyrolisis [4]. The doped nanotubes can exibit dramatic changes with respect to the undoped material. Recently Ray *et al.* [5] have reported the synthesis of silicon doped heterofullerenes in the carbon-rich limit, where the photofragmentation spectra provide a clear evidence that such clusters have Si atoms located in the fullerene network. These results are corroborated by *ab inito* calculations [6].

In this paper we present a study about isovalent substitutional impurities in carbon nanotubes. In particular, we focus on the electronic and structural properties of silicon as the substitutional atom. This doping, due to the different sizes between carbon and silicon atoms will affect locally the lattice. As is well known, silicon, as opposed to carbon, does not have the sp^2 configuration as the most stable one [7]. As a consequence there will also be, besides the simple volume relaxation, a lattice distortion that may introduce a new state in the gap, leading to the possibility that, for instance, it can be a hole or electron trap working like an amphoteric deep center. Moreover, from a structural point of view, the lone orbital due to the Si-impurity could be a center to trap other atoms or molecules. It is important to point out that there are experimental realizations of Si doping on fullerenes [8,9], which suggests that it is quite possible to also dope carbon nanotubes with Si. In the following we present an *ab initio* calculation based on the density-functional theory addressed to understand the role played by silicon doping in both metallic and semiconducting nanotubes.

METHOD

For our study of carbon nanotubes doped with Si we have used the SIESTA code [10], which performs a fully self-consistent density-functional calculation solving the standard Kohn-Sham (KS) equation. The KS orbitals are expanded using a linear combination of pseudo-atomic orbitals proposed by Sankey and Niklewski [11]. In all calculations we have used a double-zeta basis set with polarization function (DZP) [12]. The standard norm-conserving Troullier-Martins pseudopotentials [13] are utilized. For the exchange and correlation term we use the local density approximation (LDA) [14] with the parameterization of Perdew-Zunger [15]. Our calculations were performed for two types of tubes, the (6,6) metallic and (10,0) semiconductor (diameters of 8.14 Å and 7.82 Å, respectively). We use periodic-boundary conditions and the supercell approximation, with a lateral separation of 16 Å between tube centers to make sure that they do not interact with each other. For the (6,6) tube we have performed calculations using 72 atoms in the unit cell, whereas for the (10,0) tube we have considered a unit cell with 80 atoms. These unit cells have been used both for the doped and undoped tubes. We have used 8 Monkhorst-Pack k-points for the Brillouin zone integrations. The structures of the doped and undoped tubes were obtained by minimization of total energy using the Hellmann-Feynman forces with Pulay-like correction. The structural optimizations were performed using a conjugated gradient procedure until the residual forces had values smaller than 0.05 eV/ Å. In all systems studied we allowed the cell size to change after the incorporation of the Si atom.

RESULTS AND DISCUSSION

In the figure 1 we present schematically some of the Si-C and C-C relevant distances around the Si-atom. In Figs 1(a) and 1(b) we present the results for the (6,6) and (10,0) nanotubes, respectively. For the armchair (6,6) tube, the distance between a Si atom and its image in the next cell is 7.38 Å, whereas for the zigzag (10,0) nanotube it is 8.52 Å. The lengths of the unit cells along the tube direction had negligible changes in both cases (-0.3% for the (6,6) tube and 0.09% for the (10,0) tube). Observe that, concerning the three nearest-neighbors Si-C distances, there are two equivalent bond-lengths (Si-C_1 and Si-C_2 in the figure 1), and third non-equivalent bond-length (Si-C_3 in the figure 1), which is consistent with the symmetry of the system. These bond lengths are close to the Si-C nearest distance in SiC, which we obtained as 1.88 Å using a similar method of calculation. The C-C distances within a range of approximately 5 Å from the Si atom change by at most ± 1%. Concerning the displacements along the radial directions, or the bump heights, the Si atom moves upward by 0.79 Å in the (6,6) tube and 0.78Å in the (10,0) tube. In the (6,6) tube, the C_3 carbon moves upwards by 0.29 Å, whereas the two equivalent carbon atoms C_1 and C_2 move also upwards but 0.17 Å. In the (10,0) on the other hand, the C_3 atom moves upwards by 0.19 Å, whereas the C_1 and C_2 atoms move upwards by 0.27 Å. This structural behavior for the Si in nanotubes, i.e., an outward relaxation with Si-C bond lengths between 1.7-1.8 Å, is very similar to what is obtained for Si substitutional doping in fullerenes [5,6][16], as should be expected because of the similar C-bond network in these two classes of systems.
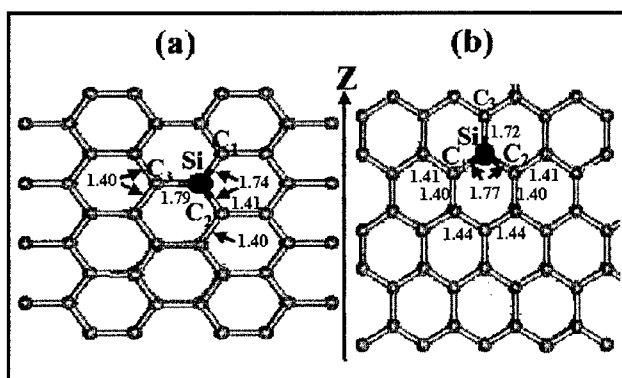
Figure 1. Some of the relevant Si-C and C-C distances (in Å) around the Si substitutional atom in the (a) (6,6) nanotube, and (b) (10,0) nanotube. The z-axis is chosen along the tube direction.

Through the total energy calculation, the formation energy (E_{Form}) is computed using

$$E_{Form} = E[tube + Si] - E[tube] - \mu_{Si} + \mu_C$$

where E[tube + Si] is the total energy of the doped tube with Si and E[tube] is the total energy for the undoped case. The μ_{Si} and μ_C are the chemical potentials for Si and C, respectively. The μ_{Si} was calculated as the total energy per atom in the Si bulk an μ_C was calculated as the total energy per atom in the undoped tubes. The formation energy was calculated for different sizes of tubes, and it nicely converges to a value of approximately 3.13 eV, which is the formation energy for the Si in the (10,0) nanotube with 80 atoms and the (6,6) tube with 72 atoms in the unit cells [17].
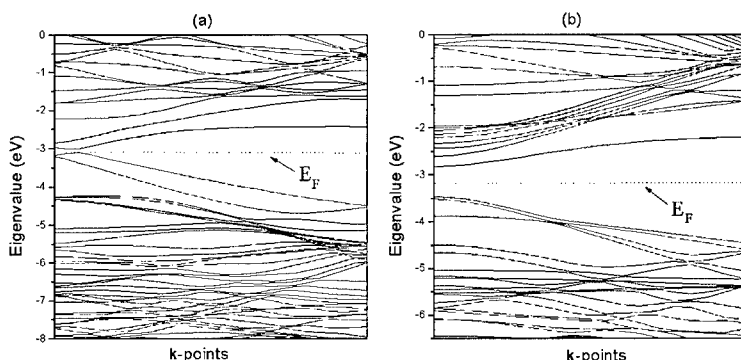
Figure 2. Band structure for carbon nanotubes with one substitutional Si (a) (6,6) tube with 72 atoms and (b) (10,0) tube with 80 atoms.
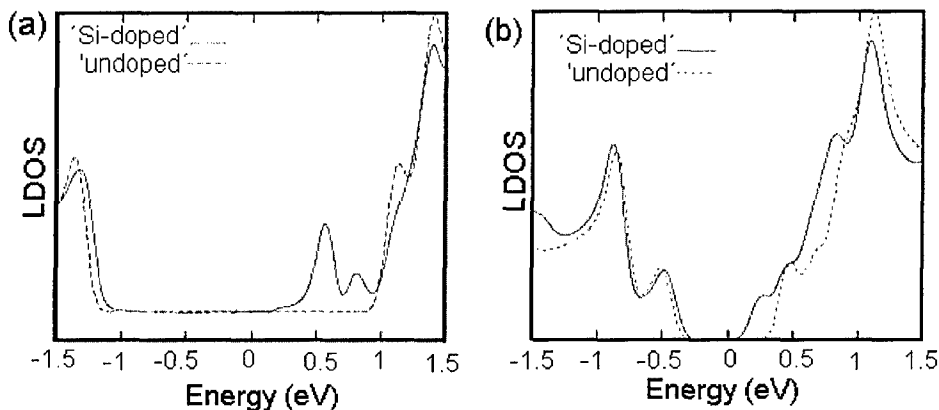
Figure 3. Electronic density-of-states (DOS) for the doped (filled line) and undoped (dashed line) nanotubes: (a) (6,6) nanotube and (b) (10,0) nanotube.

In the figure 2 we present the band structure results for the carbon nanotubes doped with silicon. For Fig 2(a) we show the (6,6) tube with 72 atoms and in Fig 2(b) the (10,0) tube with 80 atoms. The metallic tube, shows a very small gap due to symmetry break when we introduce the silicon in a finite supercell. For both system the more pronounced change due to the silicon doped is change above the Fermi-level, an empty level which is located in the foreign atom.

In the figure 3 we present the local densities of states (LDOS) around the silicon impurity for the different cases studied. For each case we report the LDOS for the doped and undoped nanotubes. The result for the (6,6) tube is shown in Fig. 3(a). As can be seen, the doping introduces two clear peaks above the Fermi level, one at 0.6 eV and another at 0.8 eV. A look at the band structure for this system shows that there is a level that starts at the Brillouin zone center, at approximately 0.8 eV above the Fermi level, which has a very small dispersion until it mixes with the pure nanotube states. There is also another band that starts at the Brillouin zone boundary with an energy of approximately 0.6 eV above the Fermi level, and also has a very small dispersion until it mixes with the pure nanotube bands. We assign these two states to a resonant Si state that gains a small dispersion due to the supercell approximation. Therefore we can conclude that Si doping (6,6) tube introduces a resonant level at approximately 0.7 eV above the Fermi level.

In the figure 4 we present the charge density for the state at the Brillouin zone boundary, located at 0.6 eV above the Fermi level. As can be seen, this state is strongly localized at the Si atom. The state at the Brillouin zone center also has a large signal at the Si atom, but shows a stronger mixing with the nanotube states, which results in a more delocalized charge density. This mixing is also observed in the charge density plot of the nanotube empty states at the Brillouin zone center close to the Fermi level.
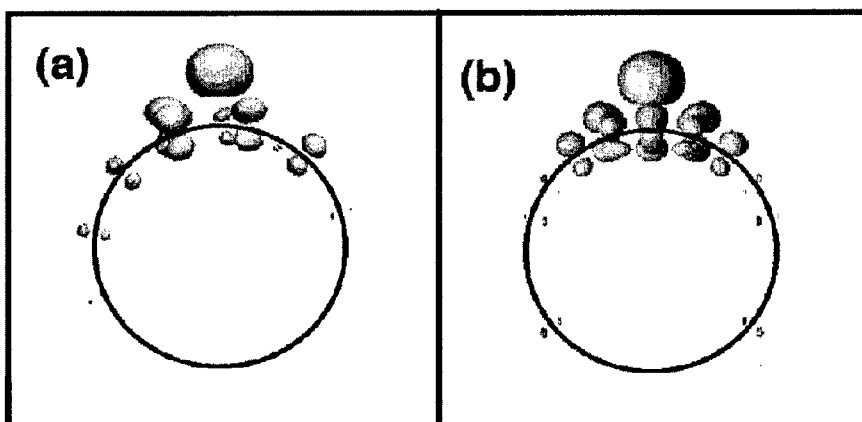
Figure 4. Electronic-charge densities for the (a) orbital at the Brillouin zone boundary located at 0.6 eV above the Fermi level, for the (6,6) doped nanotube, and (b) orbital at the Brillouin zone center located at 0.6 eV above the top of the valence band, for the (10,0) doped nanotube. The circles are guides to the eye.

The LDOS for the (10,0) tube is shown in Fig. 3(b). As can be seen, the Si introduces an empty level in the gap at approximately 0.6 eV above the top of the valence band. From the band structure calculation, we also observe this Si level in the gap, which, although the Si-Si distance is 8.52 Å, presents a small energy dispersion of order of 0.3 eV. In Fig. 4(b), the charge density for the empty level at the Γ point is shown. As can be seen, it is highly localized at the Si atom, which suggests that the silicon impurity might be an effective center to capture other atoms or molecules. A similar plot for the states at the top of the valence band shows a strong contribution from the Si atom, indicating that the Si impurity will introduce delocalized states close to the top of the valence band. It is interesting to point out that electronic structure calculations of Si doping on C_{60} [5,6][9][16] obtain that the Si introduces an occupied level very close to the highest occupied levels of pure C_{60}, as well as a level close to 0.4 eV below the lowest unoccupied levels of pure C_{60}. These findings are very similar to what we present here. However, we obtain that the levels with large Si weight, and that are close to the top of the valence bands of the pure nanotubes, are quite delocalized, as opposed to what is obtained for Si on fullerenes.

ACKNOWLEDGMENTS

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